

COMPUTATIONAL METHODS FOR ESTIMATING

PRECIPITATION FROM GEOTHERMAL BRINES

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Laboratory experiments using Salton Sea Geothermal Field brines at elevated temperatures are costly, time-consuming, and potentially difficult to perform. The LLL Geothermal Program is therefore also attempting to predict equilibria in the SSGF brines by computation.

Two approaches to this problem are being taken. Modeling of chemical reactions in the brines is being carried out using the Helgeson-Herrick (HH) code. In addition, the precipitation of many solids is being studied individually using effective activity coefficients which take chloride complexing into account.

The results of both methods are consistent with one another in predicting precipitation behavior in the temperature range 100-300°C. For example, results for Sinclair No. 4 brines at 200°C indicate that at low pH, SiO_2 , MnO_2 , and Fe silicates precipitate. As pH increases, Cu and Fe sulphides, Fe silicates and Fe oxides also precipitate.

For the San Diego Gas and Electric Magmamax brine at 200°C, the HH code predicts results quite similar to those described above for the Sinclair No. 4 brine with one notable exception, PbS precipitated at pH greater than 4.0. This correlates with observations on the scale examined from the San Diego Gas and Electric test site.

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BRINES ARE COMPLICATED

- Many Constituents
- Concentrated Salt Solutions
- Many Interdependent Equilibria
- Expensive to Experiment
- Scale Forming Components

LLL PROPOSED SCALE CONTROL METHODS

- Reduced pH (e.g., add HCl)
- Oxidize (e.g., S⁻² to S)
- Combination

CODES HELP SCREEN CONTROL METHODS

- Minimize Costly Experiments
- Save Tedious Hand Calculations
- Parameter Studies of Additives
- Account for Differences between Wells

LLL USES TWO CALCULATIONAL APPROACHES

- Helgeson-Herrick Code
Large Scale Geochemical Equilibrium Code
- Individual Solids Code
Includes Activity Coefficient for Complexes
in Concentrated Cl Solns.
Results are Mutually Consistent.

THERMOCHEMICAL CALCULATIONS

1. An approximate, or "limited reaction" method has been developed to study the chemistry of geothermal brines.
2. This method is based on the use of effective activity coefficients which take into account chlorine complexing.
3. Solubilities of scale-forming substances and distributions of non-condensable gases can be computed.
4. The effects of pH and temperature on scaling can be studied.
5. It may be possible to predict which solids will precipitate, and how much can form under specified conditions.

MINERAL SPECIES

$\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	minnesotaite (talc)	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	talc
Fe_2SiO_4	fayalite	MgSiO_3	eustatite
Mg_2SiO_4	forstersite	$\text{CaFeSi}_2\text{O}_6$	hedenbergite
$\text{CaMgSi}_2\text{O}_6$	dlopsiide	CaSiO_3	wollastonite
MnO_2	pyrolusite	$\text{Mg}(\text{OH})_2$	brucite
$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	serpentine	$\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	greenalite
MgO	periclase	$\text{Ca}(\text{OH})_2$	portlandite
$\text{Ca}_2\text{Mg}_5(\text{Si}_8\text{O}_{22})(\text{OH})_2$	tremolite	$\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	andradite
Fe_3O_4	magnetite	Fe_2O_3	haematite
CaSO_4	anhydrite	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	gypsum
MgFe_2O_4	magnesioferrite	$\beta\text{-Ca}_2\text{SiO}_4$	larnite
$\text{Mg}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	sepiolite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	ackermanite
$\text{Ca}_3\text{MgSi}_2\text{O}_8$	marwinite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	gehlenite
CaMgSiO_4	monticellite		
FeS	pyrrhotite	PbS	galena
CuS	covellite	Cu_2S	chalcocite
FeS_2	pyrite	ZnS	sphalerite
CuFeS_2	chalcopyrite	Cu_5FeS_4	bornite
Ag_2S	argentite	Cu_9S_5	digenite
NiS	millerite	HgS	cinnabar

BRINE CONDITIONS

	OXIDIZING	REDUCING
SO_4^{-2}	$2.4 \times 10^{-4} \text{ m}$	$1 \times 10^{-30} \text{ m}$
S^{-2}	$1 \times 10^{-30} \text{ m}$	$2.4 \times 10^{-4} \text{ m}$

ESTIMATED CHEMICAL DATA FOR SINCLAIR 4

RESERVOIR FLUID COMPOSITION

SPECIES	PPM	MOLS/ KG FLUID	MOLS/ KG WATER
1 AL	2.000E+00	7.412E-05	9.515E-05
2 NH4			
3 SD			
4 AS			
5 BA			
6 B			
7 BR			
8 CA	2.250E+04	5.614E-01	7.206E-01
9 CS			
10 CL	1.300E+05	3.667E+00	4.707E+00
11 CO2	4.000E+03	9.089E-02	1.167E-01
12 CU	3.000E+00	4.721E-05	6.061E-05
13 F			
14 I			
15 FE	1.150E+03	2.059E-02	2.643E-02
16 PB	7.800E+01	3.765E-04	4.833E-04
17 LI			
18 MG	5.900E+01	2.427E-03	3.115E-03
19 MN	9.500E+02	1.729E-02	2.220E-02
20 NO3			
21 K	1.160E+04	2.967E-01	3.808E-01
22 RB			
23 SiO2	4.213E+02	7.012E-03	9.001E-03
24 AG	5.000E-01	4.635E-06	5.950E-06
25 NA	5.070E+04	2.205E+00	2.831E+00
26 SR			
27 SO4	1.786E+02	1.872E-03	2.403E-03
28 S	6.000E+00	1.871E-04	2.402E-04
29 ZN			
30 TDS	2.170E+05		
31 PH	5.500E+00		

EQUILIBRIUM PARAMETERS

TEMPERATURE F	3.740E+03
C	1.800E+02
PRESSURE, PSIA	4.633E+03
ATM	1.700E+02
HPA	1.217E+01
STEAM QUALITY	1.833E+00
MASS DISTRIBUTION/KG FLUID	1.837E+01
VAPOR	
STEAM MOLS	7.642E+00
KG	1.357E-01
CO2 MOLS	9.007E-02
KG	4.000E-03
H2S MOLS	1.437E-01
ATM	1.816E-04
TOTAL MOLS	2.696E-04
LIQUID	7.633E+00
WATER MOLS	3.874E+01
KG	6.433E-01
TDS	2.170E-01

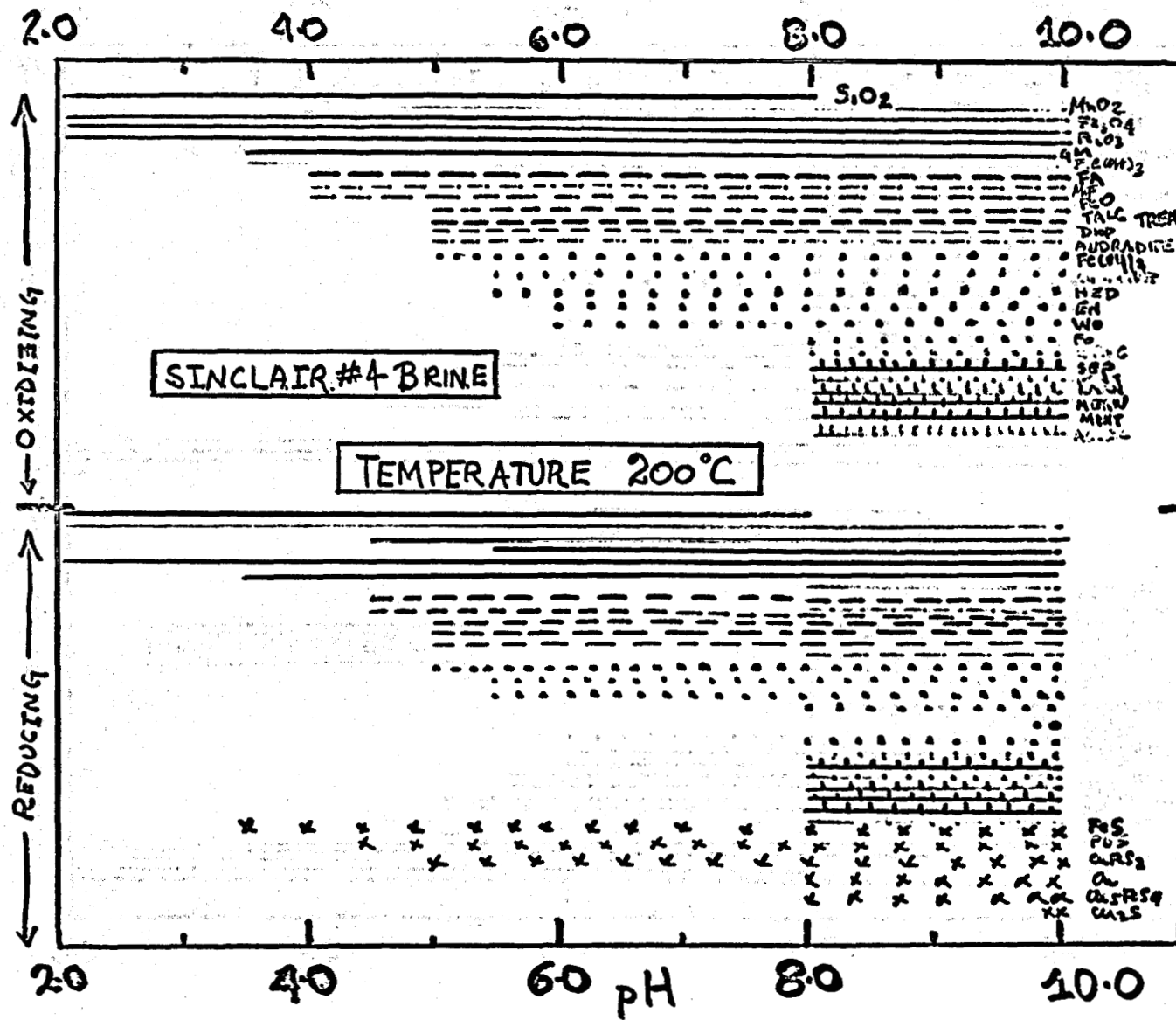


Table 1. Potential for Scale Formation from Magmamax #1 Brine

Possible Precipitation

Reducing

Al(OH)₃
CaCO₃
Cu₂S
Ag₂S
ZnS
PbS
FeS
SiO₂

Oxidizing

Fe₂O₃
CuS
CaSO₄
CuFeS₂

No Precipitation

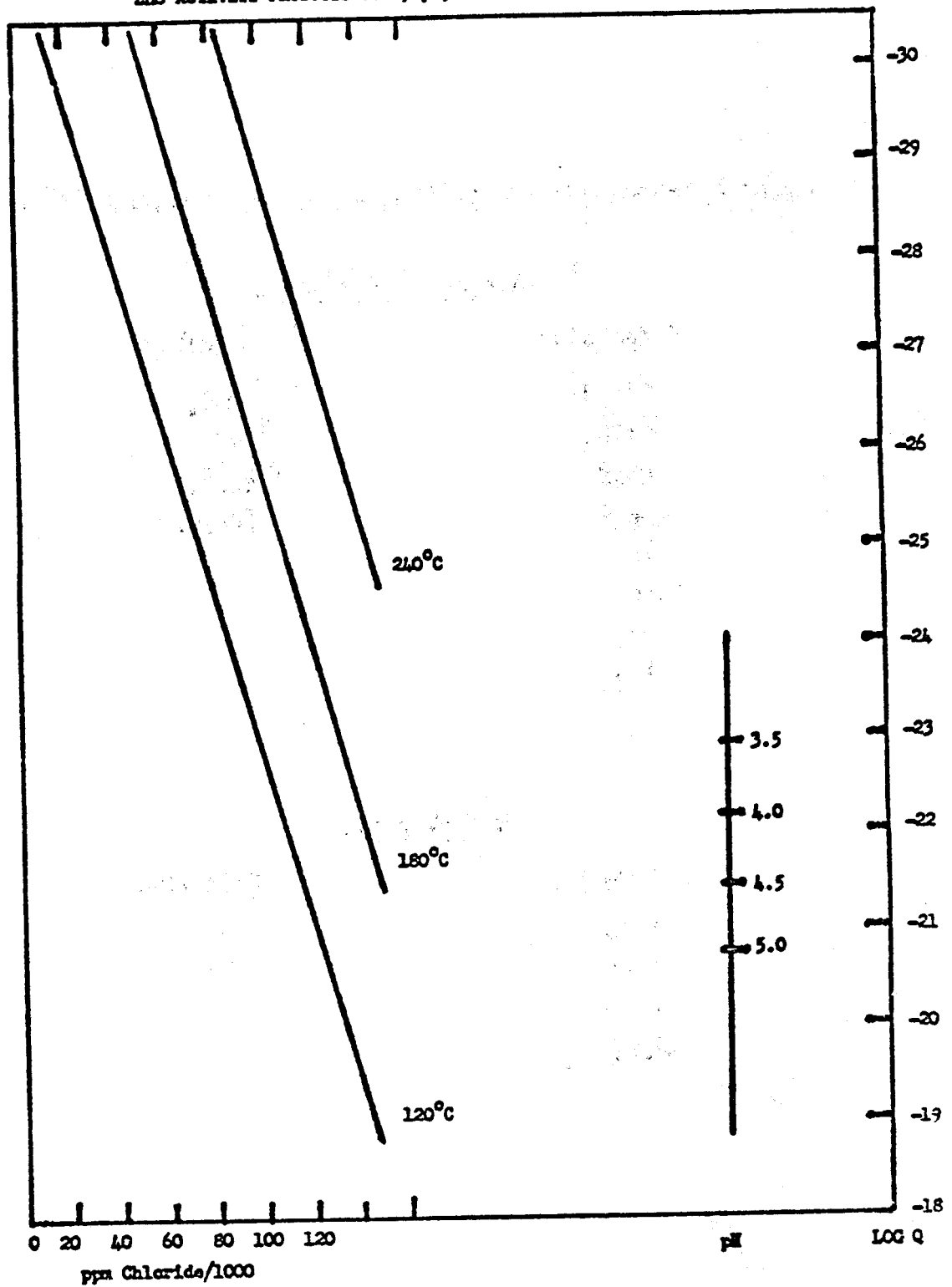
Reducing

PbCO₃
ZnCO₃
Cu₂O
Mg(OH)₂

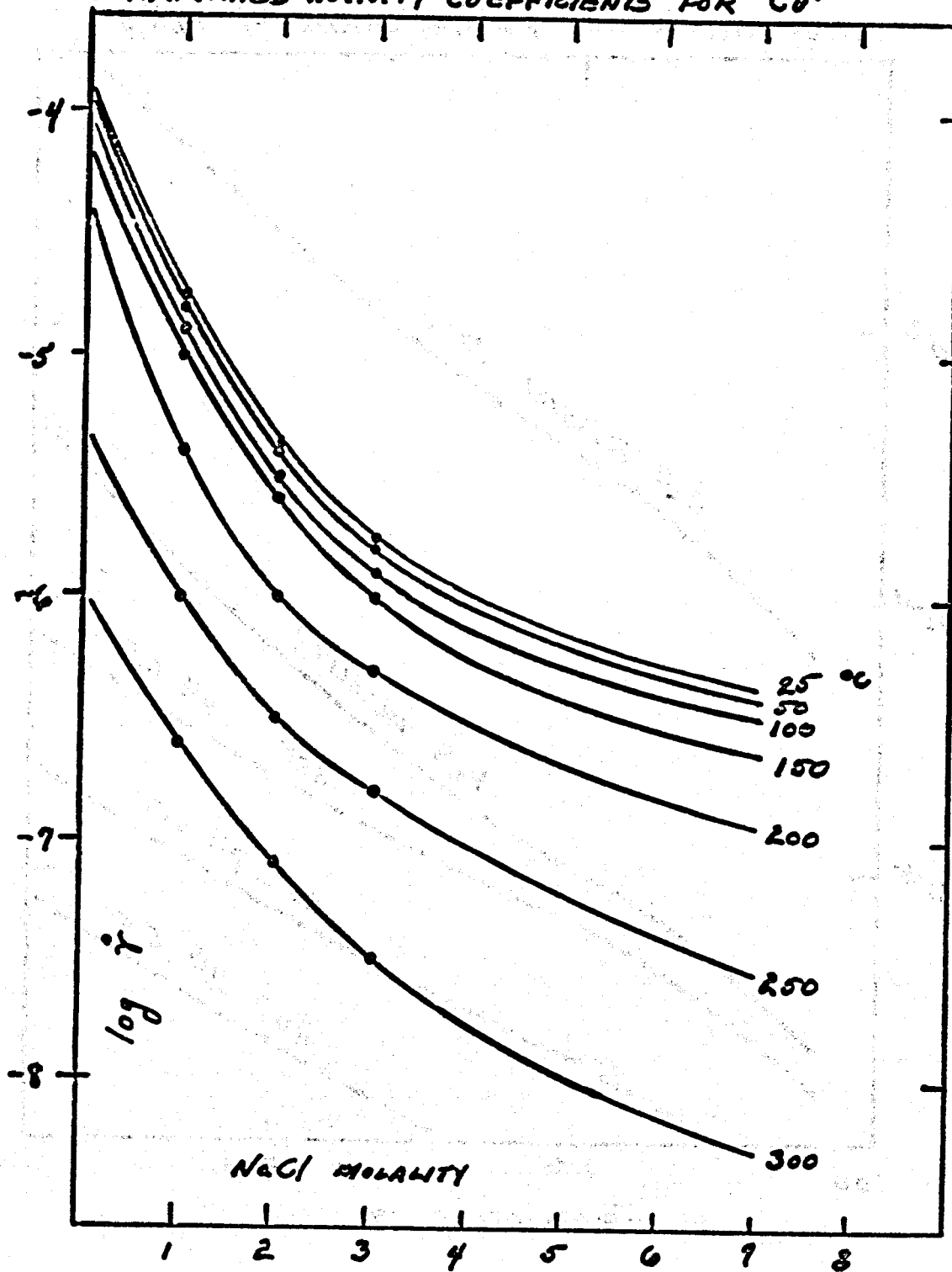
Oxidizing

CuO
PbSO₄

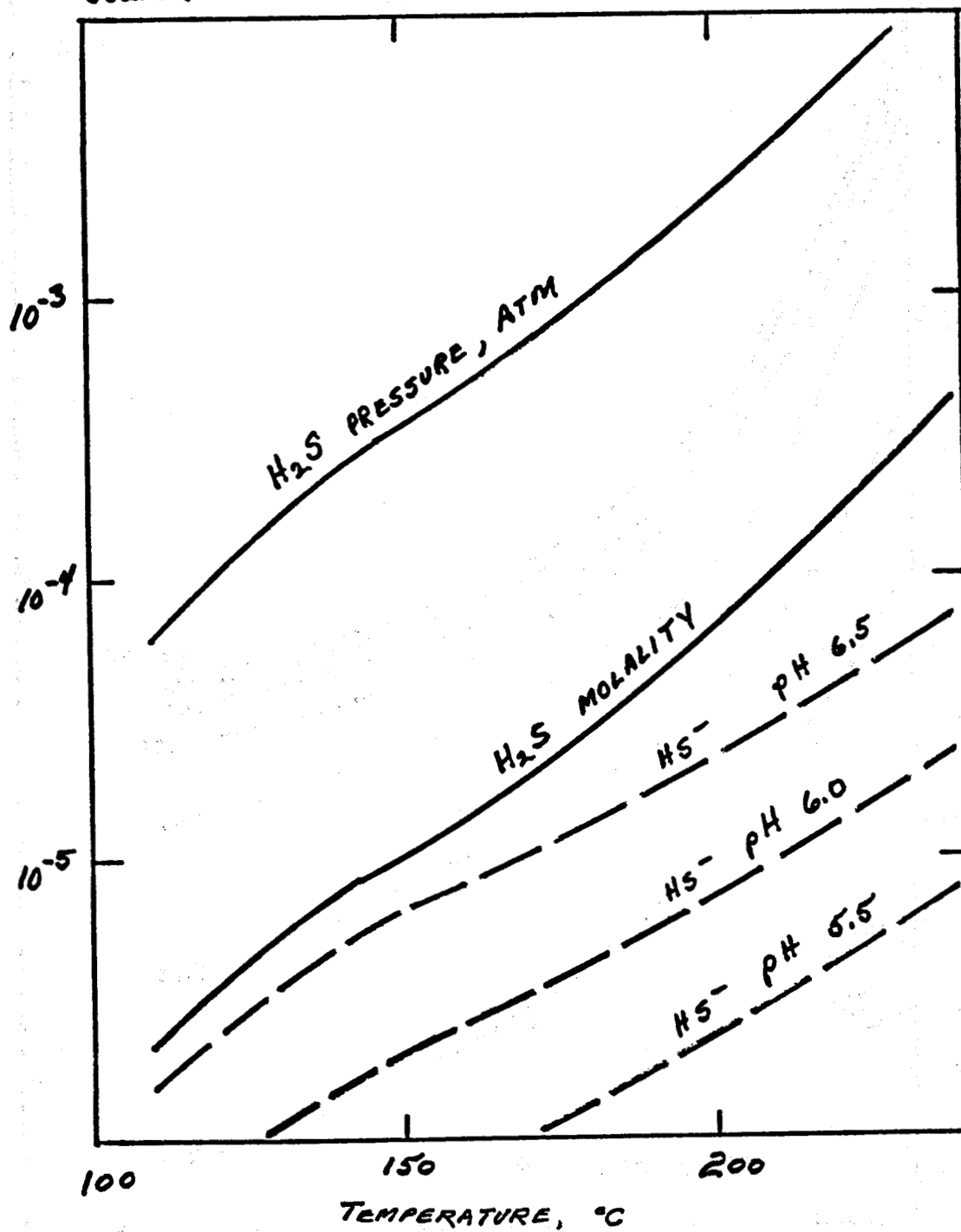
ZnS ACTIVITY PRODUCTS VS T, pH, AND Cl^-



EXTRAPOLATED ACTIVITY COEFFICIENTS FOR Cu^+

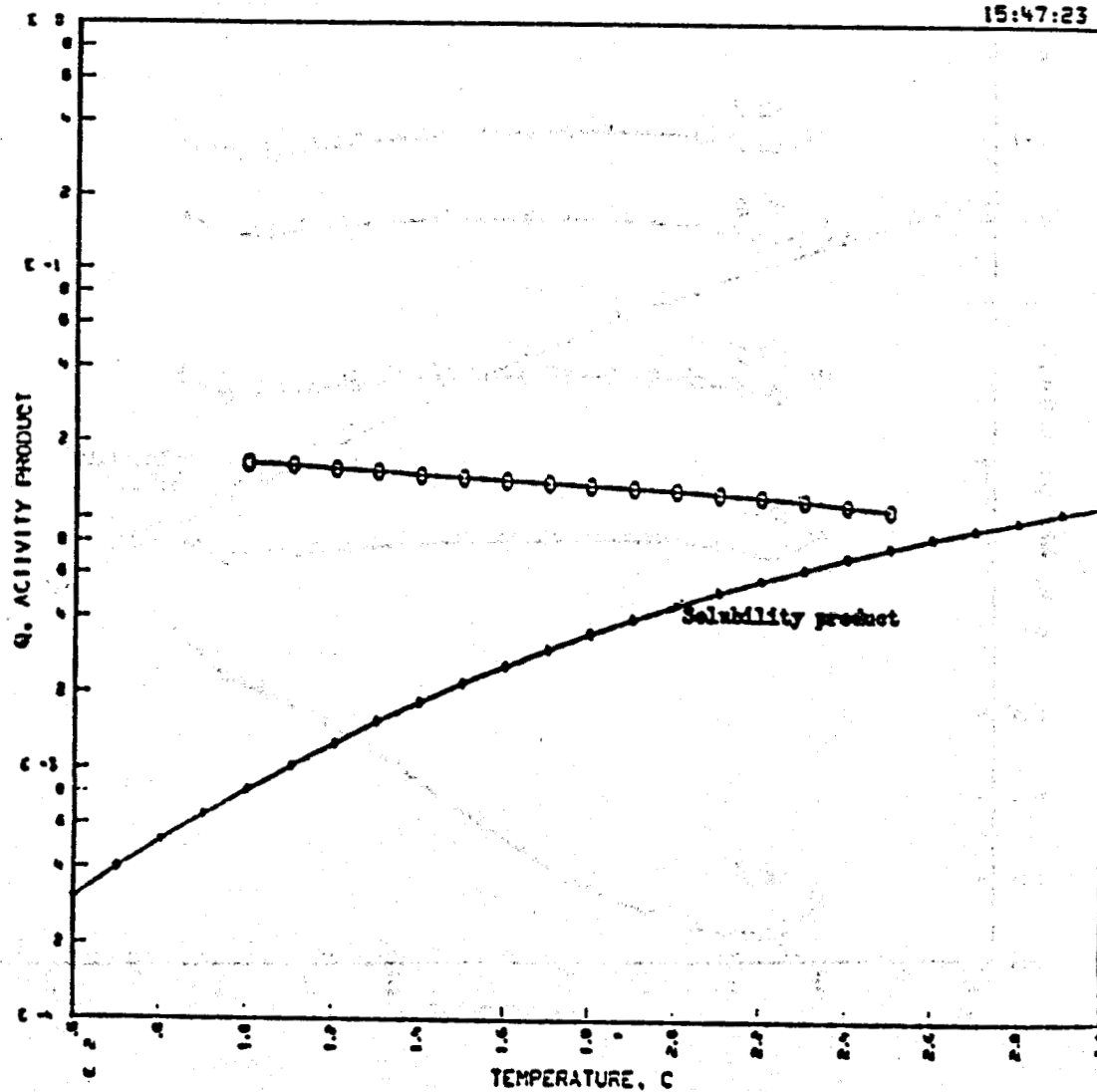


SULFUR DISTRIBUTION IN MAGMAMAX #1 FLUID



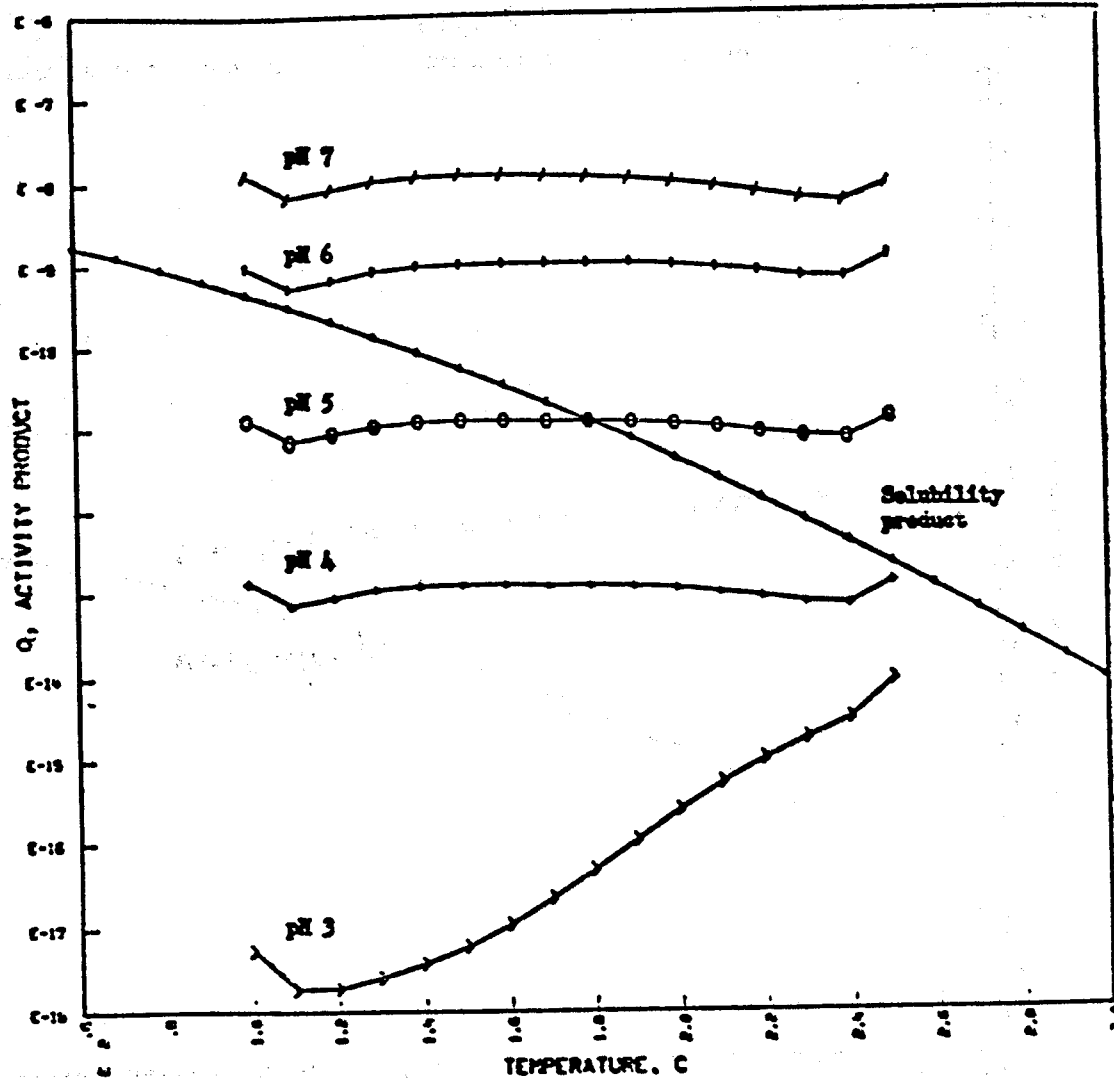
SiO₂ ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAX 1

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15:47:23



CAC03 ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAX 1

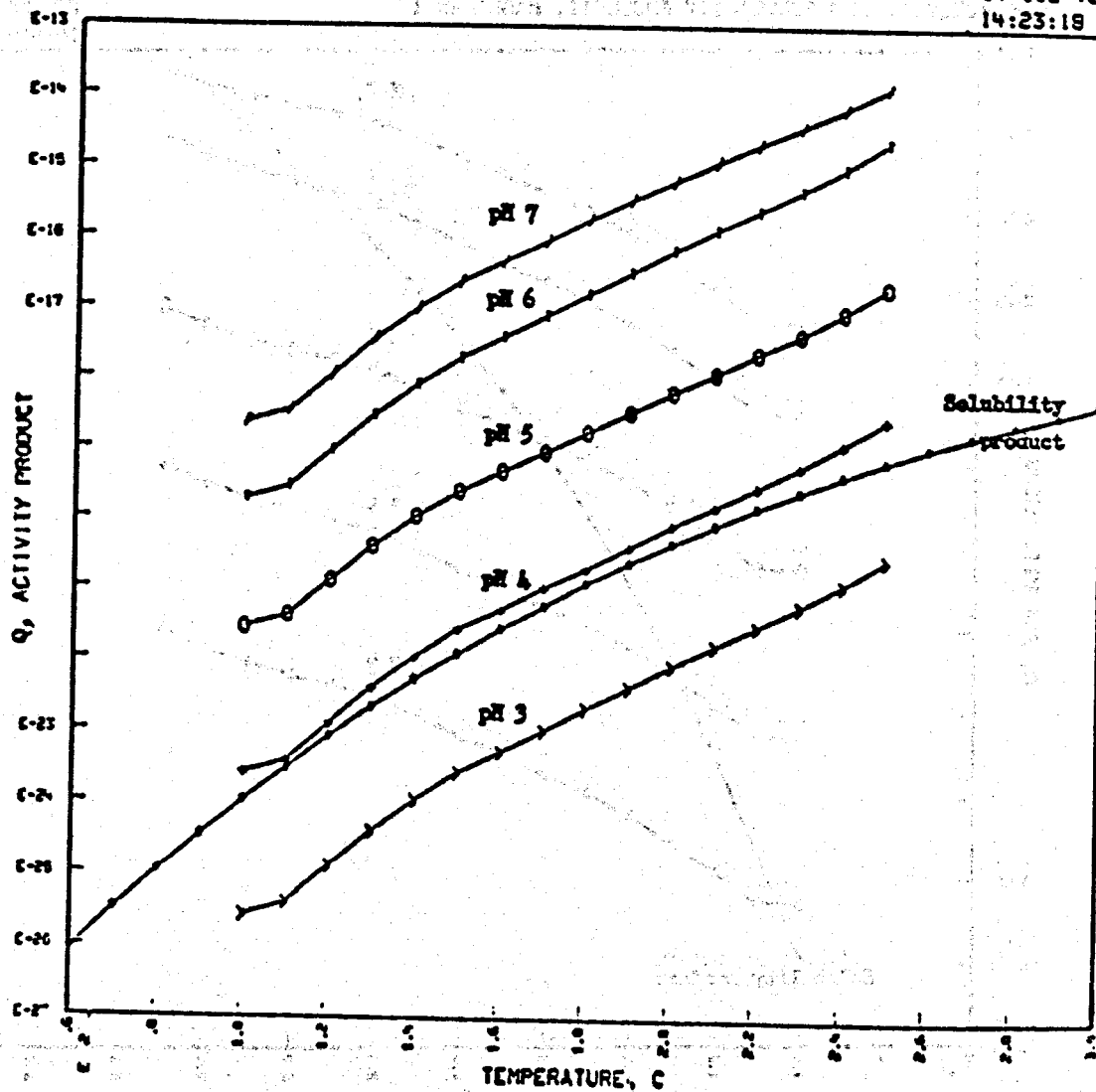
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PBS ACTIVITY AND SOLUBILITY PRODUCTS, MAGHAMAX I

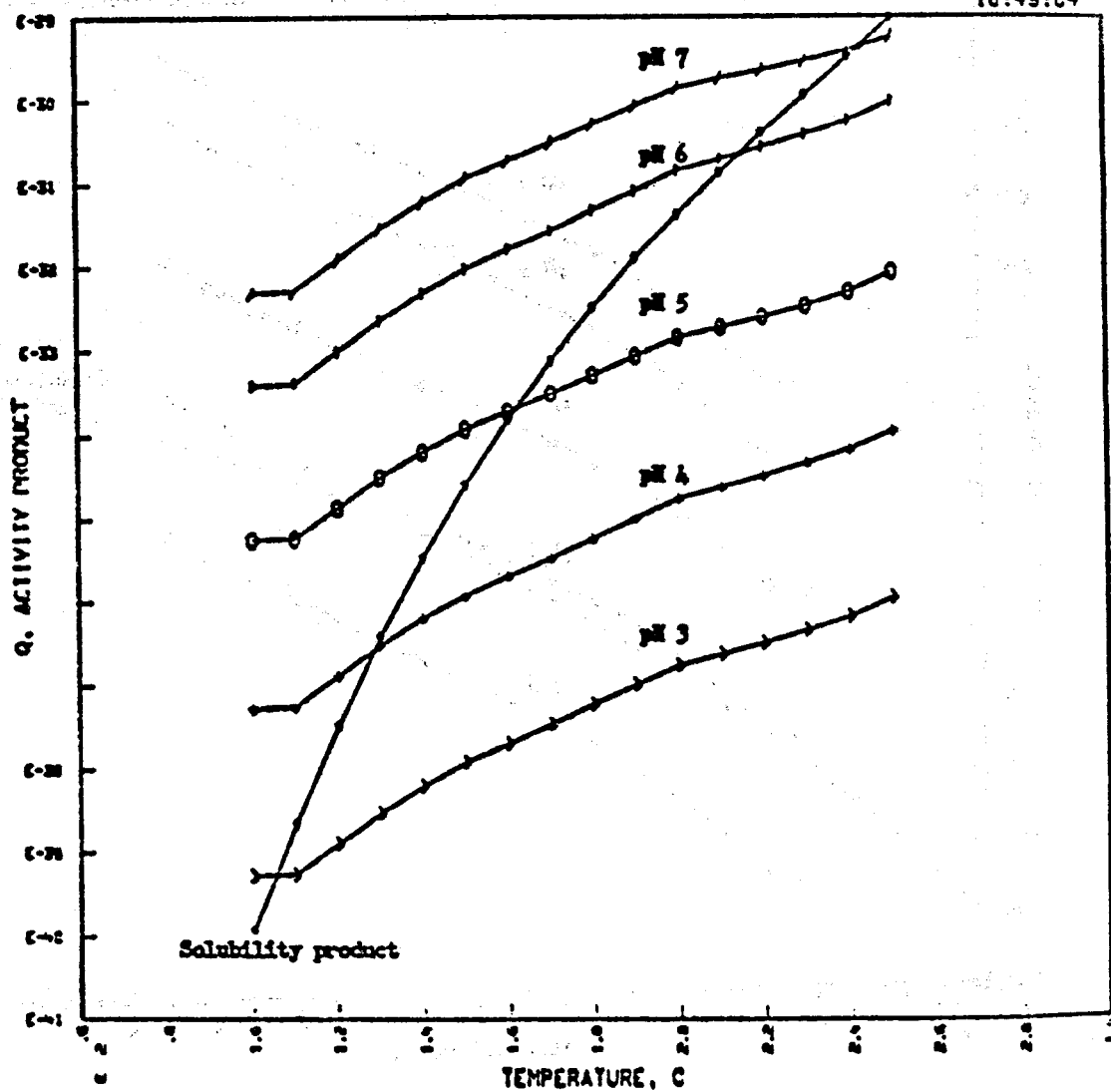
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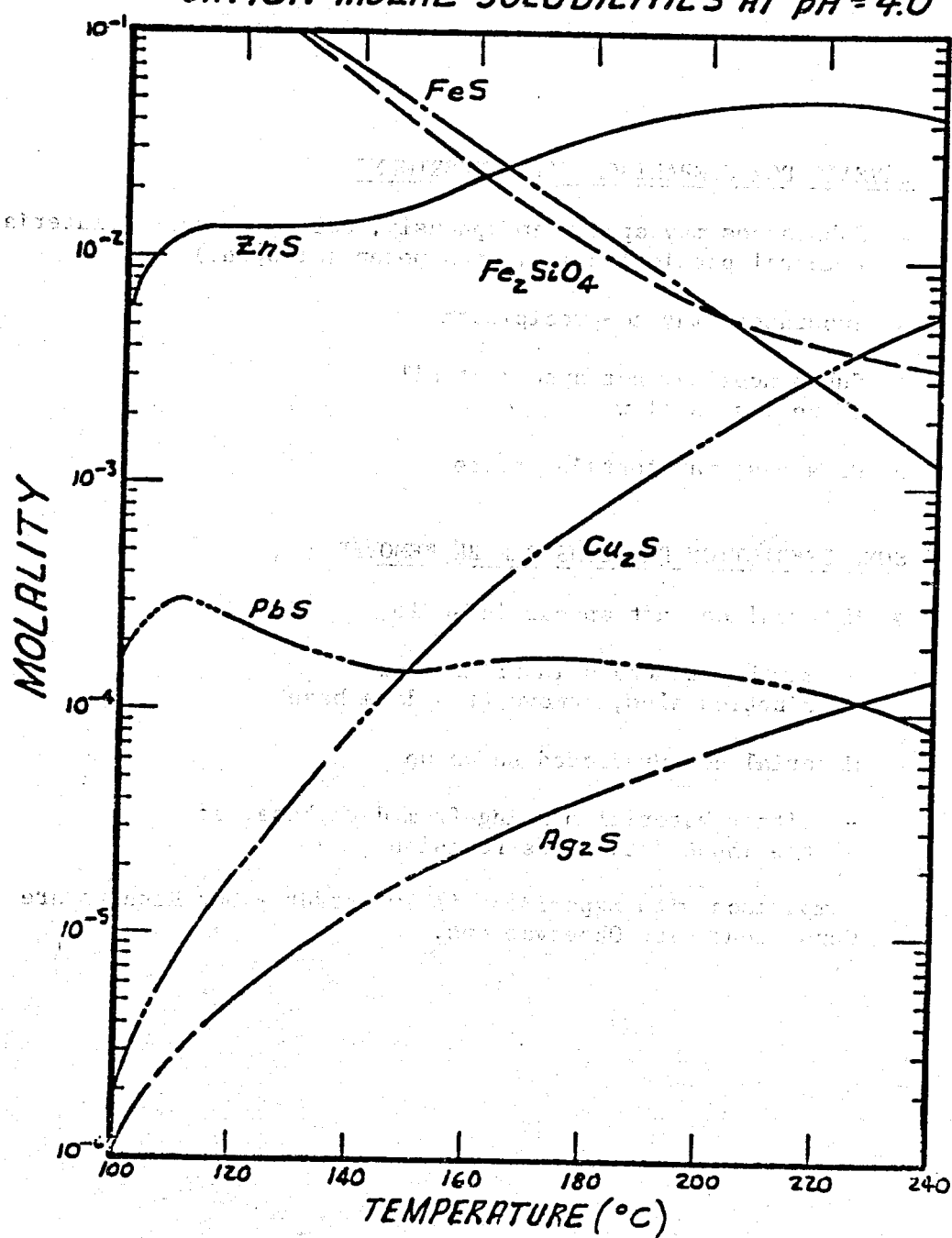


CU2S ACTIVITY AND SOLUBILITY PRODUCTS, MAGMAX 1

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10:49:04



CATION MOLAL SOLUBILITIES AT pH = 4.0



CAVEATS FOR COMPARISON WITH EXPERIMENT

- Substances may appear amorphously, not as predicted materials.
(mineral prediction indicates potential pptn.)
- Substances may co-precipitate
- Substances may not appear at all
(kinetics is slow)
- Data base may contain errors

SOME PREDICTION PROBLEMS CAN BE REMOVED

- Material doesn't appear in scale
 - may be suspended in brines; or
 - kinetics slow, remove from data base
- Material not predicted shows up
 - either material missing from data base; or
 - the input data needs revision

Comparison with Experiment is Important - Our Results are
Consistent with Observations.

NEW GEOCHEMICAL CODE IS NEEDED

- Helgeson-Herrick now
 - designed for rock soln, not solids pptn
 - doesn't yield amounts or final concentrations
 - slow with large memory requirement
- New design should be
 - fast
 - small memory
 - suitable for subroutine in other codes
 - more versatile

FUTURE APPLICATIONS

- Scale problems
 - other temperatures
 - other additives
 - other wells
- Other uses
 - corrosion (Pourbaix diagrams)
 - reinjection equilibria